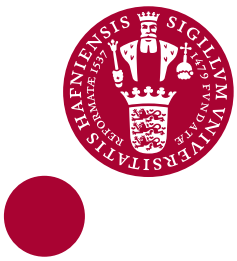

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Published in:
Geostandards and Geoanalytical Research

DOI:
10.1111/j.1751-908X.2016.00379.x

Publication date:
2016

Document version
Publisher's PDF, also known as Version of record

Vol. 40 — N° 3 09 16 P. 311 – 332

GEOSTANDARDS and GEOANALYTICAL RESEARCH

Community-Derived Standards for LA-ICP-MS U-(Th-)Pb Geochronology – Uncertainty Propagation, Age Interpretation and Data Reporting

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The LA-ICP-MS U-(Th-)Pb geochronology international community has defined new standards for the determination of U-(Th-)Pb ages. A new workflow defines the appropriate propagation of uncertainties for these data, identifying random and systematic components. Only data with uncertainties relating to random error should be used in weighted mean calculations of population ages; uncertainty components for systematic errors are propagated after this stage, preventing their erroneous reduction. Following this improved uncertainty propagation protocol, data can be compared at different uncertainty levels to better resolve age differences. New reference values for commonly used zircon, monazite and titanite reference materials are defined (based on ID-TIMS) after removing corrections for common lead and the effects of excess ^{230}Th. These values more accurately reflect the material sampled during the determination of calibration factors by LA-ICP-MS analysis. Recommendations are made to graphically represent data only with uncertainty ellipses at 2*s* and to submit or cite validation data with sample data when submitting data for publication. New data-reporting standards are defined to help improve the peer-review process. With these

La communauté internationale de la géochronologie LA-ICP-MS U-(Th-)Pb a défini les nouvelles normes pour la détermination des âges U-(Th-)Pb. Un nouveau flux de travail définit la propagation adéquate des incertitudes pour ces données, en identifiant les composants aléatoires et systématiques. Seules les données avec des incertitudes relatives à l'erreur aléatoire devraient être utilisées dans les calculs des moyennes pondérées des âges de la population; les composantes de l'incertitude pour les erreurs systématiques sont propagées après cette étape, empêchant leur réduction erronée. En suivant ce protocole amélioré pour la propagation de l'incertitude, les données peuvent être comparées à différents niveaux d'incertitude pour mieux résoudre les différences d'âge. Les nouvelles valeurs pour les matériaux de référence zircon, monazite et titanite sont définies (basée sur ID-TIMS) après les corrections du plomb commun et les effets de l'excès en ^{230}Th. Ces valeurs reflètent plus fidèlement le matériau échantillonné lors de la détermination des facteurs d'étalonnage par analyse LA-ICP-MS. Des recommandations sont faites pour représenter graphiquement des données avec seulement des ellipses d'incertitude à 2s et pour soumettre ou pour citer des

doi: 10.1111/j.1751-908X.2016.00379.x

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improvements, LA-ICP-MS U-(Th-)Pb data can be considered more robust, accurate, better documented and quantified, directly contributing to their improved scientific interpretation.

Keywords: laser ablation, ICP-MS, U-(Th-)Pb geochronology, uncertainty propagation, data reporting.

Received 18 Jun 15 – Accepted 11 Nov 15

données de validation avec les données de l'échantillon lors de la soumission des données pour publication. Les nouvelles normes de déclaration des données sont définies pour améliorer le processus d'évaluation par les pairs. Grâce à ces améliorations, les données LA-ICP-MS U-(Th)-Pb peuvent être considérés comme plus solides, exactes, mieux documentées et quantifiées, contribuant ainsi à une meilleure interprétation scientifique.

Mots-clés : ablation laser, ICP-MS, U-(Th-)Pb, propagation des incertitudes, la communication des données.

Laser ablation (LA-)-inductively coupled plasma-mass spectrometry (ICP-MS) is now a well-established analytical technique used by many laboratories world-wide. It is a diverse and flexible method for elemental concentration determination and isotope ratio analysis of a wide variety of materials. Laser ablation-ICP-MS technology has progressed rapidly in the thirty years since its inception (Gray 1985) and with improvements in mass spectrometer sensitivity, the technique is now capable of detecting attogram masses of analyte.

One application of LA-ICP-MS that has seen an explosion in interest, usage and publications in the last decade is U-(Th-)Pb geochronology, with numerous laboratories generating many thousands of these analyses each year. In this technique, very small amounts of accessory minerals (e.g., zircon, monazite, titanite, rutile, allanite, xenotime) or rock-forming minerals (e.g., calcite and aragonite) are ablated. The sample aerosol produced is transported into an inductively coupled argon plasma ion source, and the ions generated are transferred into a mass spectrometer to enable calculation of the relative isotopic abundances of U, Th and Pb contained therein. Peer-reviewed publications presenting LA-ICP-MS U-(Th-)Pb data enter the literature at an ever-increasing rate (Schoene 2014). Even so, a number of publications have highlighted the potential for inaccuracy, particularly in community results comparing interlaboratory data sets (Košler *et al.* 2013) or the equivalence of data generated using different reference materials (Gehrels *et al.* 2008, Klötzli *et al.* 2009).

U-Pb data can be collected using a range of laser and mass spectrometry equipment with the most common set-ups coupling laser systems with 266 nanometres (nm), 213 nm or 193 nm wavelengths and nanosecond (ns) pulse widths, to a quadrupole (Q-), single-collector sector-field (SC-SF-) or multi-collector (MC-) ICP-MS instrument, with any combination of these being possible and practised. In addition, femtosecond (fs) pulse-width lasers operating in the 1064 to 196 nm wavelength range are now being employed (e.g., Horn and von Blanckenburg 2007, Freydier *et al.* 2008). Each of these different analytical set-ups constrains a different acquisition methodology with different laboratories processing the resulting data through a variety of data reduction programmes (from in-house MSExcel spreadsheets to specific commercial or freely available data reduction packages), each of which uses a slightly different data reduction and uncertainty quantification procedure. With this multitude of hardware and software combinations, it is therefore not surprising that the resulting age data demonstrate variable quality (accuracy, uncertainties and, importantly, credibility of the uncertainty estimates) and ability to resolve difference between samples of similar age. This was highlighted by the study of Košler *et al.* (2013) where distinct and systematic offsets were apparent in the results from an interlaboratory comparison study of detrital zircons. Further consideration of these data, however, illustrates the consistency that can be demonstrated by some laboratories, indicating that, with the identification and elimination of systematic biases, the current uncertainty limit of LA-ICP-MS U-(Th-)Pb geochronology (*ca.* 2% 2*s*) could be significantly reduced (perhaps to *ca.* 0.5% 2*s*). This requires each laboratory to review procedures and practices to improve data quality. However, in order to identify these biases, a better understanding is required of LA-ICP-MS U-Pb data processing workflow, the acquisition parameters, the uncertainty components and their propagation.

Unlike for other isotopic systems or methods (e.g., Ar-Ar (Renne *et al.* 2009), Ge isotopes (Escoube *et al.* 2012), Mo isotopes (Greber *et al.* 2012), U-Pb TIMS (Schmitz and Schoene 2007)), the LA-ICP-MS U-(Th-)Pb community has not published recommended guidelines and standards for the handling and reporting of data in the scientific literature. As a consequence, the data and their uncertainties have not been interrogated in detail, nor has an appropriate uncertainty propagation protocol been established. This

has major implications for our ability to confidently interpret published LA-ICP-MS U-(Th-)Pb data.

With these issues in mind, an international network of practitioners (LA-ICP-MS U-(Th-)Pb Network, www.PlasmAge.org) has held a series of workshops to promote the establishment of standards and better practice guidelines for LA-ICP-MS geochronology. Guidelines for data reporting and uncertainty propagation as well as recommendations for the quantification of age uncertainties and the use of weighted mean statistics are reported here. These largely result from discussions at three workshops held in Vancouver 2008, San Francisco 2009 and Charleston 2013, with the various discussion topics led by the authors of this paper. Reports of these workshops and the consequent recommendations can be found on www.PlasmAge.org and in Horstwood *et al.* (2009, 2010) and Bowring *et al.* (2013). A workshop in Prague 2011 focussed on detrital zircon studies, and the outcomes of an associated interlaboratory comparison (ILC) exercise form the basis of a companion paper (Košler *et al.* 2013).

A note regarding errors and uncertainties

Schoene *et al.* (2013) describe the use of the terms 'accuracy', 'precision', 'error' and 'uncertainty' in U-Pb geochronology, and differentiating between these terms is useful in thinking about improving data measurement and reporting protocols. Potts (2012b) translates the International Vocabulary of Metrology (VIM 2008) guidelines and defines 'measurement error' as a 'measured quantity value minus a reference quantity value' and 'measurement uncertainty' as a 'non-negative parameter characterising the dispersion of the quantity values being attributed to a measurand, based on the information used'. Thus, an error is a single value (e.g., 0.1) and is not known unless a reference value exists to compare against. In contrast, an uncertainty is a range (e.g., 99.9 ± 0.1) that is expected to contain the true value with a given probability, often referred to as a confidence interval. Measurement error can be random (unpredictably offset from the measurand value) or systematic (consistently or predictably offset from a reference value). Once quantified, a systematic error is referred to as a bias. Each type of error has an uncertainty associated with it. These uncertainties are commonly referred to as systematic or random in reference to the error to which they relate. The uncertainty related to random error is reflected in the measurement precision ('closeness of agreement between indications or measured quantity values obtained by replicate measurements on the same or similar objects under specified conditions.' Potts (2012b)) and can be reduced by increasing the number of measurements. This standard deviation of the mean (historically referred to as 'standard error') represents the confidence in the determined average value but does not reduce the actual scatter in the data (i.e., the standard deviation of the population remains the same). The uncertainty related to a systematic error (s_{sys}) reflects how well that bias can be quantified when determined under differing conditions, that is, how reproducibly it can be measured; it cannot be further reduced simply by acquiring more measurements. The use of the term 'error' should be reserved exclusively for its defined purpose: to refer to the offset of the measurement from a mean or expected value. When referring to a confidence interval, the term 'uncertainty' should always be used.

Although it is common practice for geochemists to express uncertainties using σ, strictly this should be reserved only for statistics relating to total population (population standard deviation). Since geochemists only ever take a representative sample of a population (rather than analysing an entire pluton or, in this example, every zircon within it), the correct statistical term is *s* (sample standard deviation). We use *s* throughout this contribution where we as geochemists might usually read σ. However, both terms explicitly refer to 'standard deviation' whilst the uncertainties reported here derive from the standard error of the mean of isotope ratios, combined often with a statistical analogue of a standard deviation (the excess variance parameter described herein), ultimately combined with several other systematic uncertainties (e.g., from TIMS measurements of reference materials and from the isotopic purity and particle-counting experiments that determine decay constants). The result is neither a standard deviation nor a standard error but an uncertainty which describes the dispersion of the resulting normal distribution.

Uncertainty propagation in LA-ICP-MS geochronology

"The uncertainty of a date is no less significant than the date itself." *Ludwig (2003)*

The method used for reducing LA-ICP-MS U-(Th-)Pb data is a significant factor in the variability of results. There are numerous spreadsheet-based and software package data reduction systems in the community (e.g., LAMTrace, Jackson 2008, LAMDate, Košler *et al.* 2008, ICPMSDataCal, Liu *et al.* 2010, AgeCalc, Gehrels *et al.* 2008, Glitter, Griffin *et al.* 2008, Iolite, Paton *et al.* 2010, VizualAge, Petrus and Kamber 2012, UPb.Age (for R), Solari and Tanner 2011, U-Pb_Redux, Bowring *et al.* 2011, PepiAge, Dunkl *et al.* 2009,

UranOS, Dunkl, personal communication; etc.), all of which follow their own approach of how best to handle data from the mass spectrometer to produce a final ratio and uncertainty (e.g., Fisher *et al.* 2010, Ulianov *et al.* 2012). When reduced data are then put through weighted mean statistic and detrital provenance assessment algorithms [e.g., using Isoplot (Ludwig 2012)], they can produce different age interpretations for what was originally the same set of raw data input to the data processing packages. A workshop at the 2009 Fall AGU in San Francisco sought to address the inconsistencies in processing methods and better understand the structure and mathematical form of LA-ICP-MS geochronology data (see workshop report at www.PlasmAge.org). The aims of the workshop were to characterise and quantify:

(1) The nature and magnitude of the component uncertainties within the data – in particular the Pb/U calibration uncertainty.
(2) Which uncertainties constitute limits to the achievable level of age discrimination and therefore interpretation of the data in different contexts.
(3) The order/workflow involved in propagating these uncertainties.
(4) How this is mathematically achieved.

Recognising that similar efforts are ongoing or have been completed in the SIMS and ID-TIMS U-Pb communities (e.g., Stern and Amelin 2003, Condon *et al.* 2015), key practitioners from these communities were invited to contribute to the LA-ICP-MS effort. The structure and mathematical form of data dictate the fundamental approach by which they should be processed and a key factor in any data processing protocol is how to handle the uncertainty propagation. Uncertainty propagation protocols are currently so variable within the LA-ICP-MS community and have such a significant impact on the final interpretation that we here outline a workflow to identify and appropriately propagate the uncertainties. Standardising the approach to uncertainty propagation will help to harmonise the outputs and allow better-informed interpretations. It is not the intention of this paper to rigorously define the mathematics of the corrections, but simply to define the nature of the uncertainty components and when corrections should be made and uncertainties propagated within the process of determining a U-(Th-)Pb ratio.

Figure 1 shows the workflow for the recommended uncertainty propagation protocol (expressed as variance, s^2) for LA-ICP-MS U-(Th-)Pb data. This workflow is explained below:

1 Measure the gas blank [and calculate the uncertainty if applying an average gas blank to the whole analysis (s_{blank})]. Measure the ablation signal intensities and calculate the blank subtracted signal intensities. If correcting for common Pb on each signal intensity measurement, this correction should be made now.
2 Calculate the relevant ratios of the blank subtracted ablation signal intensities.
3 Correct for down-hole or laser-induced elemental fractionation (LIEF) (e.g., Košler *et al.* 2002, Paton *et al.* 2010).

Note that thus far the data have been handled at the signal integration level only.

4 If using a 'mean of ratios' approach, calculate the mean of the individual ratios along with the corresponding standard deviation of the mean (s_{m1}*).

If using a 'ratio of means' approach, calculate the ratio of the mean of two blank-corrected signal intensities and quadratically add the standard deviation of the mean for each of the two signal peaks in the ratio (s_{m1}*).

For a description of the difference between these two approaches see Fisher *et al.* (2010); each approach offers some benefits over the other depending on count rates of the analysis and instrumentation used to acquire the data. However, any differences are eliminated when using geometric means (rather than arithmetic means) as advocated for compositional data (Aitchison 1986, 1999). This overcomes bias in the data resulting from low total counts, due to either low concentration sample material or short duration signal integration.

If using an average gas blank propagate the gas blank uncertainty. If using an interpolated gas blank (e.g., Paton *et al.* 2010), the uncertainty contribution is allowed for in step 5.

5 At this point, the data should be corrected for drift and normalised to the primary reference material. Taking the data population for this reference material (or ideally a secondary reference material after normalisation), the excess variance (scatter) (ε^2) should be defined for the $^{206}Pb/^{238}U$ ratio and the $^{207}Pb/^{206}Pb$ ratio (and the $^{208}Pb/^{232}Th$ and

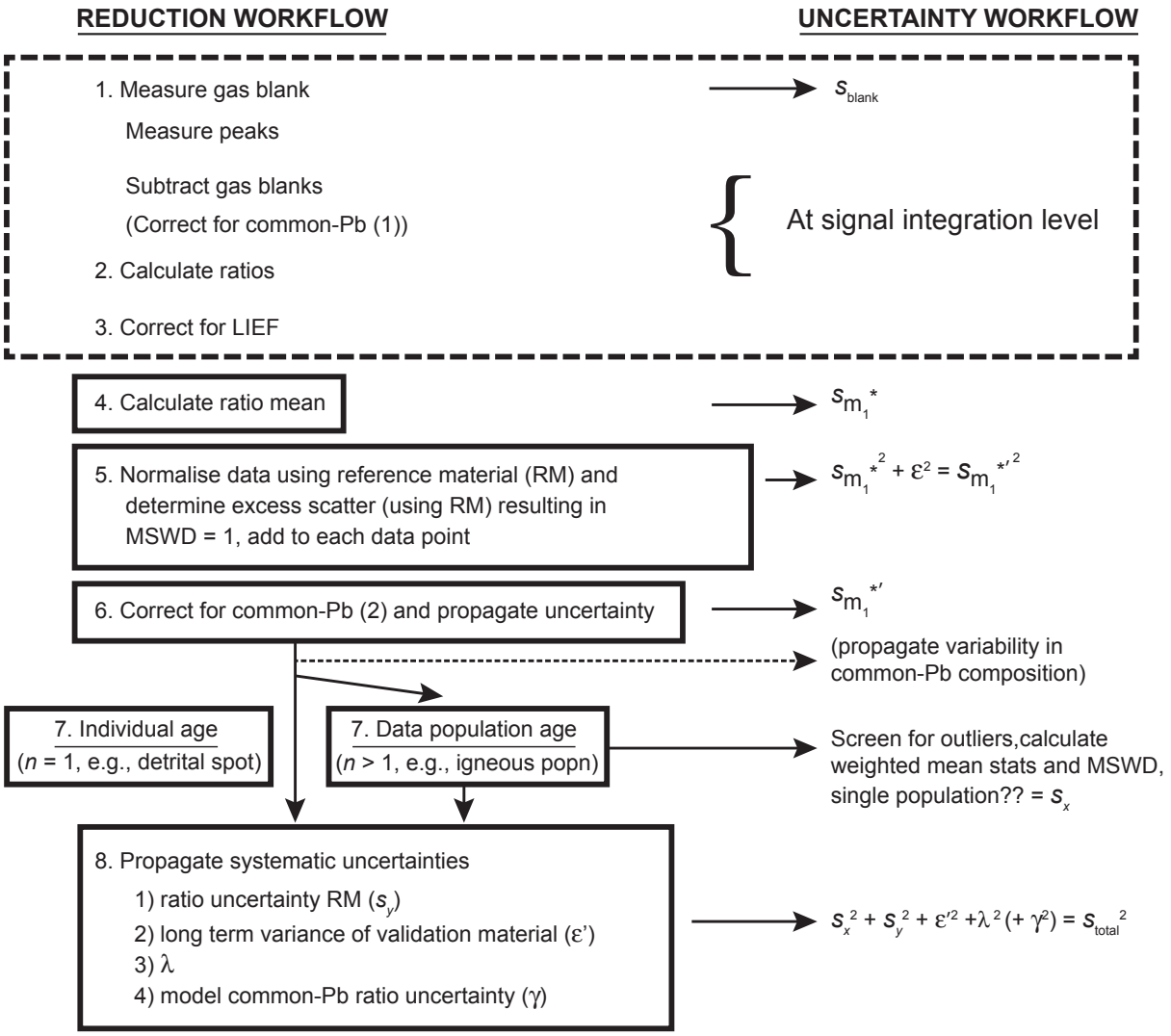

Figure 1. Schematic illustration of the defined uncertainty propagation workflow.

$^{208}Pb/^{206}Pb$ ratios for Th containing minerals). This is the uncertainty component, additional to the measurement uncertainty, required to make the reduced chi-squared value [also known in geochronology as the mean squared weighted deviation (MSWD, Wendt and Carl 1991)] of the weighted mean population equal to 1. The assumptions here are that the data population for the reference material represents a single population and that the excess variance represents the variance between measurements not accounted for in the measurement uncertainties of the individual determinations. For the $^{206}Pb/^{238}U$ ratio, this is largely due to the variable fractionation behaviour of the interelement ratio during the measurement session and can be appropriately quantified using the primary reference material data population corrected for drift (see Paton *et al.* 2010 for further explanation and Figure 2 of this study). For the $^{207}Pb/^{206}Pb$ ratio, however, the excess variance will only be revealed when the measurements are sufficiently precise and this requires larger ion beam signals, ratios nearer unity that are easier to measure and appropriate dwell times. Since for any set of data the dwell times are usually fixed, ion beam signals and the magnitude of the ratio become the key factors. Except for very young ages, the former will likely be more dominant. The $^{207}Pb/^{206}Pb$ excess variance can be estimated simply by taking a number of measurements whilst ablating a range of spot sizes on a reference material to vary the ^{207}Pb signals measured, thereby defining a calibration curve for excess variance versus ^{207}Pb

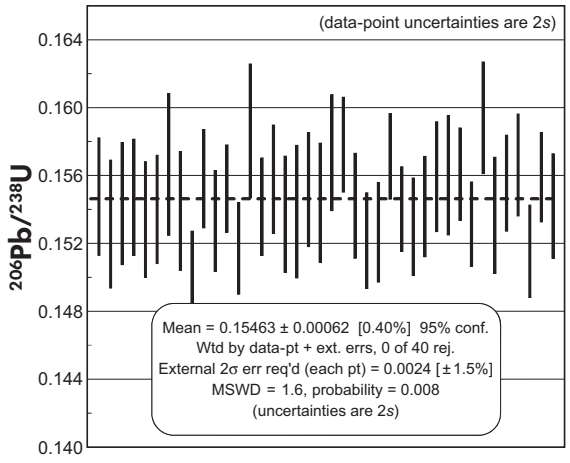

Figure 2. An example of a weighted average calculation generated using Isoplot (v. 4.14) to determine the excess variance for the 91500 zircon reference material. The excess variance is indicated as the 'External 2σ err req'd (each point)'. In this example 1.5% (2*s*), additional variance is identified, which should be propagated into sample and validation material data point uncertainties. Note: For demonstration purposes, the Isoplot-generated terminology has been retained (also in Figure 3a) to highlight the differences of usage in this paper.

intensity. NIST glass could be used for this, as in experiments performed to characterise SIMS Pb-Pb performance (Stern and Amelin 2003). It should be noted that the determination of this Pb-Pb excess variance needs to be performed by each laboratory since the exact amount of additional uncertainty will vary with the dwell times and ablation duration used by the operator. In the case of MC-ICP-MS, this might be near zero (*ca.* 0.1% 2*s* in Figure 3a). The excess variance should be propagated into the data point uncertainty for each sample and validation material ($s_{m1}{}^{*\prime}$), in the case of the $^{207}Pb/^{206}Pb$ ratio, according to the size of the measured ^{207}Pb signal for each data point (Figure 3b). If no excess variance is exhibited by the primary reference material, no additional uncertainty propagation is required for that session.

6 If a common Pb correction is made based on the average common Pb measurement for the whole of the ablation/selection (e.g., 30 s), the correction should now be made and the appropriate uncertainty propagated. If a common Pb correction has been made using compositions based on independently measured values (e.g., feldspar Pb) or a composition likely to be variable within the host material, then this common Pb compositional variability/uncertainty should be propagated now. If a model Pb composition is being used (e.g., Stacey and Kramers 1975), this propagation comes later (see step 7).

7 It is now appropriate to assess the data populations and screen for outliers. If the data represent detrital mineral grains, where each grain is assumed to have been sourced separately, this obviously does not apply. If the data are expected to represent one or more events (e.g., igneous and metamorphic crystallisation events), the data populations should be screened for outliers and assessed as to whether they represent a single population using weighted mean statistics and MSWD. Assuming that the weighted mean of the population has an MSWD around 1 (the range of acceptable MSWD values varies according to the number of data points in the calculation, see Wendt and Carl 1991), the resulting uncertainty (s_X) represents a valid assessment of the uncertainty on the defined mean *at the level of the data point uncertainty* (see section 'Use of weighted mean statistics in LA-ICP-MS geochronology and the role of systematic uncertainties') and can be used in quantifying the difference to other data determined at the same time (see section 'The quotation and comparison of dates and ages'). 'Populations' with MSWD › 1 (i.e., outside of acceptable limits) represent scatter in the data not attributable to measurement uncertainty alone and should not be quantified using a weighted mean statistic. If the assumption of single population status is considered valid (based on other information sources), then this excess variance should be propagated into the data point uncertainty before applying a weighted mean calculation with the recognition that the data have a low resolution of conforming to the assumption and that the age uncertainty will be limited by the data point uncertainty (see section 'Use of weighted mean statistics in LA-ICP-MS geochronology and the role of systematic uncertainties'). Regardless, the MSWD value (and number of data points) should be quoted with the weighted mean statistic to demonstrate the coherence of the data set on which the statistic was based.

8 Having obtained s_X, representing either the detrital data point uncertainty or igneous/metamorphic population uncertainty, systematic uncertainties should now be propagated to quote the result as an age. These uncertainties are:

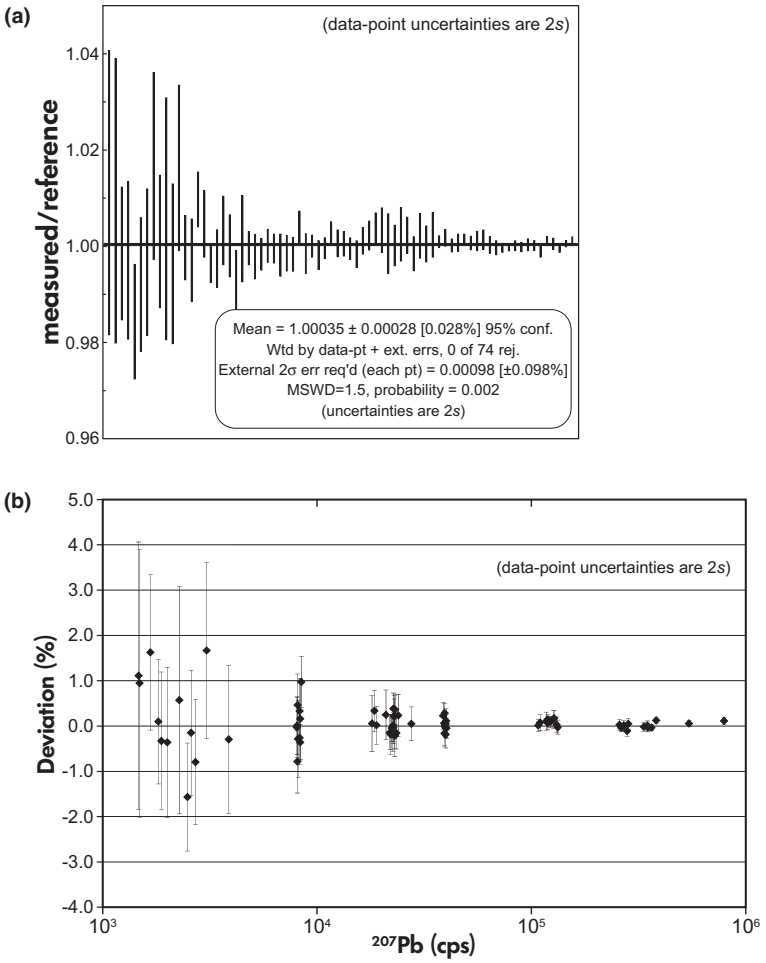

Figure 3. (a) Deviation (as the measured/reference ratio) for $^{207}Pb/^{206}Pb$ of NIST SRM 612 and 614 for a series of ablation spots (15–50 μm, 4 J cm^{-2}, 10 Hz), demonstrating no apparent linearity issues and an excess variance ('External 2σ error' of Isoplot) for the data population of *ca.* 0.1% 2*s*. This characterises the additional uncertainty that should be added to each data point during this measurement session for the $^{207}Pb/^{206}Pb$ uncertainty. Data point uncertainties are 2*s*. (b) The same data as in (a) expressed as deviation (%) relative to the ^{207}Pb signal intensity in counts per second (cps). Data point uncertainties are 2*s*.

(a) ratio uncertainty of the primary reference material used for normalisation (s_Y)
(b) long-term excess variance of the validation materials (ε′)
(c) decay constant uncertainties (λ)
(d) model Pb ratio uncertainty (e.g., Stacey and Kramers 1975) used for the common Pb correction if based on the measurement average (γ).

These uncertainties are propagated now since systematic uncertainties constitute limiting uncertainties (the uncertainty level below which the final uncertainty cannot be quoted) and cannot be reduced by increasing the number of data points. By including these uncertainties earlier in the propagation, they would be reduced erroneously during the definition of the population uncertainty (s_X). Note that the uncertainty related to systematic errors must be applied to the ratio uncertainty before calculation of the age uncertainty.

Currently, for LA-ICP-MS U-Pb geochronology, the long-term excess variance (ε′) of $^{206}Pb/^{238}U$ is the most significant uncertainty related to systematic error (*ca.* 2% 2*s*). Ideally, this would be monitored using a relatively high U and Pb concentration reference material to most precisely resolve the excess variance. However, since homogeneity of available reference materials is an issue (see section 'Reference values and constants'), the material considered by the laboratory to be most homogeneous should be used. Note then that a precisely measured heterogeneous validation material will

lead to an overestimation of ε′ whilst a low precision determination of ε′ will result in underestimation (assuming that even the most homogeneous material is heterogeneous at some level).

The final age uncertainty of the detrital data point or sample population is represented as a quadratic addition of all these components with γ weighted according to the size of the common Pb correction. The resulting final uncertainty we define as s_{total}.

Use of weighted mean statistics in LA-ICP-MS geochronology and the role of systematic uncertainties

> *"MSWD-values... distinguish between systems... where the analytical precision does or does not permit demonstration of the geological scatter."*
>
> *Kalsbeek (1992)*

> *"...improved precision has highlighted systematic analytical biases and uncovered geologic complexity that affects mineral dates."* *Schoene et al.* (2013)

> *"Even in the best cases, the reported age uncertainty will not be much better than the analytical error [sic] of the most precise analyses. [This] accords with the concept that the real limit on accuracy for U/Pb dates is only a factor of two or so better than the analytical error [sic] of the individual analyses, rather than amenable to arbitrary improvement by increasing the number of analyses alone. This concept follows statistical limitations on the ability to resolve complexity in the true age structure of a suite of analyses arising from open system behaviour, presence of xenocrysts, or a variable and non-zero magma-residence-time."* *Ludwig (2012)*

Weighted mean calculations reduce the variance of a population by square root of *n taking into account the data point uncertainties*. The data point uncertainties define the MSWD or 'goodness of fit' of the data to the weighted mean (better known in the rest of the science community as the 'reduced chi-squared statistic'). The key target is to obtain an MSWD value around 1 for a weighted mean of a data population, indicating that the data population reflects a single discrete value. However, in line with the Kalsbeek (1992) quote above, since scatter cannot be resolved below the level of the data point uncertainties, *the assumption of a single population,* required by the weighted mean statistic, *is only valid at the level of the data point uncertainty.*

The data point uncertainty therefore represents a limiting factor in the interpretation of geological age, much below which a mean value cannot be stated as conforming to the assumptions used to define it (Ludwig 2012).

Equally, interlaboratory bias is also a factor in this complexity. Including systematic uncertainties in the data point uncertainties prior to establishing, the presence of a single population masks the ability to resolve any variation. An apparent normal distribution is then more readily achieved but can only be quoted as normal at the level of the data point uncertainties. Using a weighted mean statistic on a data set, the uncertainties of which contain systematic components, therefore leads to the averaging of complex variation and results in overly precise age uncertainty quantifications. Spurious differences between populations are then interpreted, leading to overconfidence in the level of achievable age resolution.

A detailed LA-ICP-MS example of this is illustrated in Sláma *et al.* (2008) in characterising the Plešovice zircon reference material. In the case of at least one of the laboratories participating in this study and likely all, systematic uncertainties (included in the standard deviation of the primary reference material) were built into the data point uncertainty propagation for the LA data and resulted in weighted mean ages outside of uncertainty of each other in two of the three cases. Although considered appropriate by the community at the time, reconsideration of our uncertainty propagation protocol leads us to now understand that this approach reduces erroneously the systematic uncertainty component within the data, which should represent a limit below which the final uncertainty cannot be stated. Taking this into consideration, and assuming for each of the participants a 1.2% (2*s*) ε′ stated by one participant in Sláma *et al.* (2008), Table 1 illustrates the likely level of the uncertainty when the uncertainty propagation protocol defined here is used.

The resulting newly calculated uncertainties after propagation for systematic components demonstrate that the LA-ICP-MS results of Sláma *et al.* (2008) from all laboratories were probably in agreement within their appropriate uncertainties. This also illustrates how reporting all relevant information when publishing data increases the lasting value of data sets so that they might be re-interpreted in the light of new information and ideas (see section, 'The reporting of LA-ICP-MS U-(Th-)Pb data').

Table 1.
Example recalculation of the LA-ICP-MS age uncertainties reported for the Plešovice zircon in Sláma *et al.* (2008)

	Sláma *et al.* (2008) result	Estimated new uncertainty
Laboratory A	339.0 ± 2.0	339.0 ± 4.5
Laboratory B	335.0 ± 1.0	335.0 ± 4.0
Laboratory C	338.0 ± 1.0	338.0 ± 4.1

The uncertainty propagation is applied to the ratio uncertainty not the age uncertainty; X% of a ratio does not equal X% of an age due to the non-linearity of the age equation.
Age units are Ma.

Reference values and constants

When processing LA-ICP-MS U-(Th-)Pb data, a primary reference material is used to calibrate or 'correct' the data for the sample and validation materials. To obtain accurate results, it is vital that reference values for the primary material are well characterised (generally determined by isotope dilution methods) and that these values appropriately describe the *actual* material ablated. For example, zircon can lose radiogenic Pb, and monazite can incorporate variable amounts of common Pb and/or build up excess ^{206}Pb due to the incorporation of extra ^{230}Th at the time of crystallisation. For these reasons, it is not valid to ask the question 'What is the age of the reference material?' In detail, this will vary depending on whether one is describing the ^{207}Pb/^{206}Pb, ^{206}Pb/^{238}U, ^{207}Pb/^{235}U or ^{208}Pb/^{232}Th date, or the 'concordia age' (Ludwig 1998), which represents a statistical weighting of two of these. Instead, it is the relevant isotope ratio that must be used to normalise the corresponding data for the sample and validation materials. A reference ratio including or excluding common Pb and/or ^{230}Th corrections should be used depending on whether this correction has been made to the LA-ICP-MS data at this point.

Although ID-TIMS data are the benchmark reference data for LA geochronology, it should be noted that these data are typically tabulated as *ratios* corrected for common Pb with *dates* additionally corrected for ^{230}Th disequilibrium. Unless these corrections have already been made to the reference LA data (and this is generally not the case), these ages and ratios will be the *wrong* reference values to use for calibrating LA-ICP-MS analyses. By example, using the data of Wiedenbeck *et al.* (1995), zircon 91500 consistently demonstrates slight discordance, resulting in a lower ^{206}Pb/^{238}U ratio (and age, 1062.4 Ma) than would be expected if assumed concordant at the age given by its

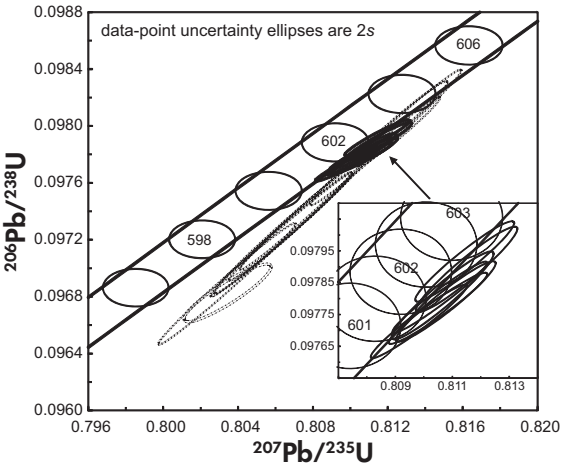

Figure 4. Wetherill concordia plot showing data for the zircon reference material GJ1 from Jackson *et al.* (2004) (dashed ellipses) and this study (bold ellipses) with inset highlighting the more concordant data from this study.

^{207}Pb/^{206}Pb ratio (1065.4 Ma). This represents a potential 0.3% inaccuracy in one of the normalisation factors if only one of these ages is assumed to represent the correct 'age' of the material. A larger effect is demonstrated for GJ1; here, the difference in the respective ages represented by the ^{206}Pb/^{238}U and ^{207}Pb/^{206}Pb ratios is 1%. New ID-TIMS U-Pb data for GJ1 (see Table S1, online supporting information) obtained using chemical abrasion (Mattinson 2005), the EARTHTIME tracer (McLean *et al.* 2015, Condon *et al.* 2015) and the ^{238}U/^{235}U ratio defined in Hiess *et al.* (2012), replicate the results of Jackson *et al.* (2004) (without chemical abrasion; see Figure 4) but with significantly greater precision, demonstrating that this sample is measurably discordant. Consistent apparent discordance must be reflected in the reference values used for normalising LA-ICP-MS data. The cause of this discordance sits outside of the scope of this discussion, but at least in part stems from inaccuracy in λ^{235}U relative to λ^{238}U (Schoene *et al.* 2006, Mattinson 2010). The same features can be seen in monazite reference material data where common Pb and excess ^{206}Pb from initial ^{230}Th disequilibrium result in an otherwise reversely discordant 'Stern' monazite being 'concordant' at an age older than its true age (*ca.* 512 Ma vs. 507 Ma, Figure 5, Table 2). This 'concordant' material is, however, the composition of material sampled during laser ablation analysis and therefore provides the correct reference ratios that should be used to define normalisation factors if common Pb and Th corrections are not to be applied to the data prior to normalisation.

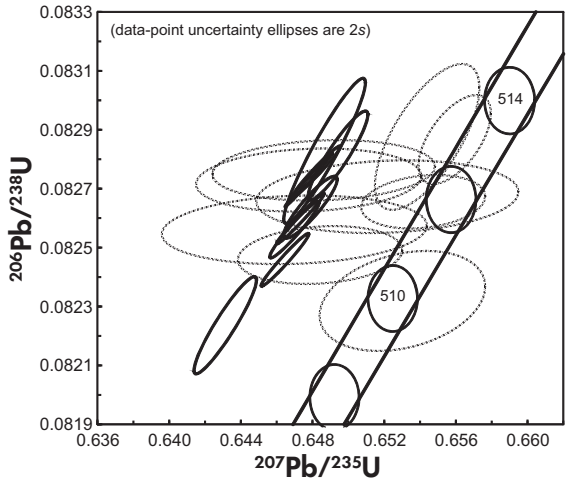

Figure 5. Plot of ID-TIMS data for the 'Stern' reference monazite. Ellipses with bold lines are the data published in Palin *et al.* (2013), fully corrected for common Pb and Th. Ellipses with dashed lines are the same data without corrections for common Pb and Th. The 'Stern' monazite was acquired from Richard Stern, GSC, Ottawa; its sample number is 8153 and is sourced from the Bananeira I Pegmatite in Brazil.

Thus, a detailed examination of zircon and monazite reference materials demonstrates that a single 'reference age' should not be used to derive expected U/Pb, Th/Pb and Pb/Pb ratios for a material. Instead, the ID-TIMS determined ratio uncorrected for initial common Pb and ^{230}Th disequilibrium should be used (assuming that these corrections have not already been made to the laser ablation data). The example of GJ1 also demonstrates that if a single reference age is taken as the concordia age of the ID-TIMS data set, both Pb/Pb and U/Pb reference values will be inaccurate, because the concordia age is not equivalent to either ratio value.

Table 2 (also available as supporting information as Table S2) presents preferred reference values and uncertainties for these materials that should be used in deriving normalisation factors for LA-ICP-MS data standardisation. Values are reported with and without correction for common Pb and without correction for excess ^{230}Th in all instances. Included here are new CA-ID-TIMS data for Mud Tank (Table S1), which reproduce the result achieved by Black and Gulson (1978) but with a tenfold improvement in uncertainty on the newly determined age of 731.65 ± 0.49 Ma (95% conf., ^{206}Pb/^{238}U weighted mean age, MSWD = 1.9, n = 6). However, it should also be noted that some materials used as reference materials (e.g., GJ1 and various 'Sri Lanka' zircons) have been suggested to be heterogeneous at the crystal scale, with different crystals potentially having different ratios to those results published as reference values. Ideally, each crystal of a reference material should be characterised separately or, as in the case of the Temora 1 and 2 multiple crystal reference materials, intercrystal isotopic homogeneity should be demonstrated as far as is practically possible (Iles *et al.* 2015). The data in Table 2 are therefore given as an advance on previously published values in the absence of capability for an individual laboratory to define reference values for the material they have at hand. The CA-ID-TIMS source data for the recalculations shown in Table 2 are given in Table S1.

Since a number of non-zircon U-containing minerals are required as reference materials but show variable common Pb contents (e.g., Chew *et al.* 2014), a preferable way of defining the reference material compositions is through 'reference models' which have this variability built into the calculations (see McLean *et al.* in press). It is also noted that the Th-Pb age of a mineral need not be concordant with its U-Pb age (Seydoux-Guillaume *et al.* 2012), the experience of most practitioners using Manangotry monazite, for example.

Additionally, following the high-precision U-Pb EARTHTIME initiative to better determine some of the fundamental constants and sources of uncertainty in U-Pb data (Hiess *et al.* 2012, Condon *et al.* 2015), it is recommended that the new ^{238}U/^{235}U value of 137.818 ± 0.045 (95% conf.) (Hiess *et al.* 2012) be used routinely to replace '137.88' when describing the modern day U isotope ratios typically found in zircons and calculating ^{207}Pb/^{235}U ratios. Although this might seem to make a trivial difference for an average zircon (*ca.* 0.035% in the ^{207}Pb/^{235}U age at 500 Ma), Hiess *et al.* (2012) highlighted more aberrant ^{238}U/^{235}U values in monazites and titanites as well as in some zircons. In fact, two of the more commonly used monazite and titanite reference materials, Moacyr monazite (Seydoux-Guillaume *et al.* 2002) and Fish Canyon Tuff titanite (Schmitz and Bowring 2001), are cited by Hiess *et al.* (2012) as having the lowest (137.743) and highest (138.490) ^{238}U/^{235}U values, respectively, of all the terrestrial accessory minerals they analysed. These different U isotope ratios would result in ^{207}Pb/^{235}U age differences of *ca.* -0.2 Ma to +2 Ma for a *ca.* 500 Ma mineral compared with using a ^{238}U/^{235}U value of 137.818. With increasing interest in non-zircon accessory phase LA-ICP-MS geochronology and the lack of well-characterised reference materials for this purpose, it is important to recognise the potential for systematic error caused by variable ^{238}U/^{235}U compositions. For example, in determining cooling and uplift rates by dating different phases in comparison to zircon, it becomes important to be confident of this ratio. In the absence of this confidence and being forced to assume 137.818 as the ^{238}U/^{235}U of the

Table 2.
Reference values for some reference materials commonly used in LA-ICP-MS U-Pb dating

Reference material	*n*	Radiogenic ratios[a]						Ages						Hiess *et al.* (2012)
		$^{207}Pb/^{206}Pb$	± %	$^{207}Pb/^{235}U$	± %	$^{206}Pb/^{238}U$	± %	$^{207}Pb/^{206}Pb$	±	$^{207}Pb/^{235}U$	±	$^{206}Pb/^{238}U$	±	$^{238}U/^{235}U$
GJ1	7	0.060139	0.031	0.81117	0.065	0.097860	0.065	607.70	0.67	603.11	0.30	601.86	0.37	137.824
Mud Tank	6	0.063802	0.048	1.0569	0.11	0.120188	0.071	734.4	1.0	732.29	0.55	731.65	0.49	137.836
Plešovice	10	0.053244	0.027	0.39396	0.057	0.053694	0.034	337.96	0.61	337.26	0.16	337.16	0.11	137.803
91500 xl	7	0.074941	0.030	1.8525	0.066	0.179365	0.040	1066.01	0.61	1064.32	0.44	1063.51	0.39	(137.818)
Stern	6	0.056872	0.037	0.64715	0.14	0.08261	0.25	484.68	0.81	506.73	0.57	511.7	1.2	137.763
Moacyr	2	0.056824	0.072	0.64831	0.13	0.082830	0.064	482.5	1.6	507.44	0.52	512.99	0.31	137.743
Ontario 2	6	0.074373	0.11	1.820	0.60	0.17753	0.61	1050.7	2.2	1052.6	3.9	1053.5	5.9	(137.818)
Reference material	***n***	**Ratios with initial Pb[b]**						**Ages**						**Hiess *et al.* (2012)**
		$^{207}Pb/^{206}Pb$	± %			$^{206}Pb/^{238}U$	± %	$^{207}Pb/^{206}Pb$	±			$^{206}Pb/^{238}U$	±	$^{238}U/^{235}U$
GJ1	7	0.060171	0.08			0.097877	0.07	608.8	1.8			601.95	0.40	137.824
Mud Tank	6	0.06402	1.0			0.12021	0.14	741	21.4			731.8	1.0	137.836
Plešovice	9	0.05332	0.19			0.053707	0.04	341.6	4.4			337.24	0.13	137.803
91500 xl	7	0.074989	0.075			0.17942	0.07	1067.3	1.5			1063.78	0.65	(137.818)
Stern	6	0.05735	0.26			0.08265	0.29	504.1	5.7			511.9	1.5	137.763
Moacyr	2	0.0613	3.8			0.08327	0.36	648[$]	32			515.6[$]	1.0	137.743
Ontario 2	6	0.1187	1.9			0.1874	0.66	1935	33			1107.4	6.7	(137.818)

All samples have been annealed and chemically abraded after Mattinson (2005).

Uncertainties are 2*s* in all cases; percent for ratios, absolute for ages. $^{207}Pb/^{235}U$ ratios calculated using $^{238}U/^{235}U$ after Hiess *et al.* (2012) (or 137.818 average where not directly determined). Calculations are based on the decay constants of Jaffey *et al.* (1971). $^{206}Pb/^{238}U$ and $^{207}Pb/^{206}Pb$ ages NOT corrected for initial disequilibrium in $^{230}Th/^{238}U$.

All zircon values based on CA-ID-TIMS results shown in the Supporting information. Values for Plesovice based on a recalculation of data in Slama *et al.* (2008) as shown in the Supporting information.

Values for Stern and Moacyr based on data in Palin *et al.* (2013).

Values for Ontario 2 based on data in Spencer *et al.* (2013). Values given are weighted averages expanded to reflect scatter where appropriate; [$]values are averages and range (taking into account data point uncertainties) due to low *n*.

[a] Corrected for fractionation, spike, and common Pb; up to 1 pg of common Pb was assumed to be procedural blank: $^{206}Pb/^{204}Pb = 18.60 \pm 0.80\%$; $^{207}Pb/^{204}Pb = 15.69 \pm 0.32\%$; $^{208}Pb/^{204}Pb = 38.51 \pm 0.74\%$ (all uncertainties 1*s*). Excess over blank was assigned to lab blank for zircons or initial Pb for non-zircon phases.

[b] Corrected for fractionation, spike, and blank Pb only.

mineral of interest, the potential for systematic error should be considered with respect to the final age defined and therefore the geological interpretation. In addition, Hiess *et al.* (2012) indicated that rock type seemed to be governing the extent of $^{238}U/^{235}U$ fractionation, the implication being that the same mineral phases from different rock types at the same or different localities may falsely appear different in age if they have different $^{238}U/^{235}U$ ratios.

Most recently, the use of chemical abrasion (thermal annealing plus partial dissolution; Mattinson 2005) in LA-ICP-MS geochronology has been highlighted as improving concordance and repeatability of U-Pb ratio measurements (Allen and Campbell 2012, Crowley *et al.* 2014, von Quadt *et al.* 2014). The thermal annealing of zircon results in increased structural coherence, reducing ablation rate, LIEF and the potential variability of LIEF. Other authors have shown that improved U-Pb repeatability may not result (Marillo-Sialer *et al.* 2014) and, in the case of monazite, chemical abrasion increases the age and compositional variability of the material (Peterman *et al.* 2012). If thermally annealed/chemically abraded reference materials are used, sample materials ought also to be treated similarly to try to maintain the structural similarity of sample and reference materials that is required for accurate calibration of LA-ICP-MS U-Pb data. However, the behaviour of materials during thermal annealing and chemical abrasion relates to the uranium concentration of the material and the time duration over which radiation damage has accumulated (i.e., a function of age and α-recoil dose rate). Different zones of a zircon crystal may have become completely metamict (altered to baddeleyite and silica) and will not re-form as coherent zircon during thermal annealing. For this reason, the effect of thermal annealing on data quality will likely be variable between samples and thus, for unknowns, it will be difficult to determine whether improved accuracy has been achieved or not. Regardless of whether annealed/not annealed (or chemically abraded) reference materials are used, the correct reference values should be used for data normalisation. However, most high-precision ID-TIMS laboratories now produce only chemically abraded data for zircons, which could result in systematic biases if samples are not also chemically abraded (note the more concordant CA-ID-TIMS 91500 data in Table S1 compared with the non-CA data in Wiedenbeck *et al.* 1995). If the LA-ICP-MS community requires reference data without chemical abrasion, specific requests for this will need to be made. Inherently, this will mean accepting lower accuracy (less precise) reference values from the point of view of the geological age of the material, but these will be more accurate (less biased, assuming material homogeneity) with respect to the actual isotopic composition of the material ablated.

The quotation and comparison of dates and ages

Following the proposed uncertainty propagation for LA-ICP-MS U-(Th-)Pb data, it is clear that data can be compared, in some situations, without some systematic uncertainty propagation. It is stressed that the assessment that the data set comprises a single population must still be performed at the uncertainty level defined prior to step 8 above, and that to do so with any of the additional systematic uncertainties would invalidly reduce the apparent scatter. The following conditions apply:

(1) Data points and data populations generated within the same measurement session can be compared at the level of s_X to more easily discriminate between populations/points. This includes plotting detrital data for one rock sample. Since these uncertainties are not fully quantified (do not contain systematic components), these data are not absolute and therefore can be compared only to each other.
(2) Data points and data populations generated in the same laboratory but measured over two or more analytical sessions and normalised using the same primary reference material can be compared using $s_X + \varepsilon'$, or $s_X + \varepsilon' + s_Y$ if using a different primary reference material. This includes, for example, the comparison of detrital data generated in different sessions for a suite of samples.
(3) When comparing data points and data populations generated in different laboratories or from publications and databases, uncertainties at the level of s_{total} should be used. With full systematic uncertainty propagation, these results are absolute and traceable to the SI (assuming an unbroken chain of quantification).

Schoene *et al.* (2013) summarised the distinction between a 'date' and an 'age' citing the former as 'a number calculated using measured isotopic ratios and the decay equation' with a date becoming an age when 'geological significance' is assigned to it. Adding to this, single data point results are therefore dates whilst accumulation of a number of these is generally required to define an age. The accumulated data may remain a date if not considered to be of geological significance (e.g., a calculated result determined on material having suffered Pb loss).

Now that we can compare data at different uncertainty levels, it is important to consider at what level of uncertainty the data should be reported for publication. It is recommended that *ratio data* be tabulated in all instances without

the propagation of uncertainties related to systematic error (s_{sys}), but that data point *'date' uncertainties* be reported at the level appropriate to the study. For materials where multiple data points are being used to define an age (e.g., for igneous and metamorphic studies), the 'date' uncertainties should be tabulated without propagation for uncertainties relating to systematic error. A summary table of determined sample *ages* and their fully propagated uncertainties is considered essential to a manuscript reporting LA-ICP-MS U-(Th-)Pb data. For detrital studies, within-sample, within-grain (i.e., core vs. rim) and within-session comparison requires omission of the systematic uncertainty components to resolve variation, whilst these sample data will ultimately be compared with data produced in another session, laboratory or in the published literature and this comparison requires the inclusion of systematic uncertainty components. For this reason, it is recommended that data columns for date uncertainties be included with and without s_{sys} in the data-reporting table (see Table 4). Systematic uncertainty components should be quantified in the table footnotes at all times so that published final propagated population age uncertainties can be reproduced.

In metamorphic and igneous petrogenetic studies, it is common to discriminate between multiple samples analysed within and between sessions and to make a comparison to other data in the literature. As demonstrated above, in order to achieve this, specification of the different levels of uncertainty propagation is required. However, even when comparing within-session results, it would be helpful still to make reference to the total uncertainty of the absolute result to demonstrate whether quoted age differences exceed the systematic uncertainty level or not. To represent this, it is recommended that final ages be quoted with two levels of uncertainty, α and β, as follows: 'Age $\pm$ α/β' at the 2*s* level, where $\alpha = s_X$ and $\beta = s_{total}$. In this way, it will be immediately apparent at what level of confidence the two ages are the same or different. This is similar to practice in the ID-TIMS U-Pb community where quotation of three levels of uncertainty is recommended (Schoene *et al.* 2006). Ultimately, age uncertainties should be quoted at the level of $2s_{total}$. Uncertainty representations less than this are relative only to a stated reference (e.g., with respect to another sample).

The graphical representation of U-Pb data

For a single measured parameter (univariate data) that is assumed to be normally distributed, the true value is expected to lie within 2*s* of the estimated mean ~ 95% of the time. However, U-(Th-)Pb data are typically presented as ellipses on a Wetherill (1956) or Tera and Wasserburg (1972) concordia plot, combining two variables that share a joint bivariate normal distribution. Only 86% of the data lie within a 2*s* uncertainty ellipse (see Figure 6), and only 39% of the data from the two variables fall within a 1*s* ellipse. It is more likely therefore that the true data point lies outside of the 1*s* ellipse than within it. For this reason, it is strongly recommended that data on concordia plots (or plots for any bivariate data, e.g., isochron diagrams) are always plotted at the 2*s* level. This represents a more robust and transparent graphical representation of the true range within which a data point is likely to lie without requiring the reader to envision a doubling of the 1*s* uncertainty ellipse area or to replot the data, to see if two data points might overlap within 2*s*.

Accuracy and precision in LA-U-(Th-)Pb data

Laser ablation-ICP-MS U-(Th-)Pb geochronology is currently a low precision analytical technique (1–2% 2*s* for U/Pb) when compared with CA-ID-TIMS (< 0.1%); a function of the smaller amount of material sampled (*ca.* 35–70 ng for LA *cf.* 0.5 μg for TIMS), the lower detection efficiency of the method (*ca.* 0.1–0.4% Pb LA-ICP-MS *cf.* 5% Pb TIMS) and the occurrence of biases the causes of which remain as yet incompletely understood. As such, its ability at present to resolve small degrees of analytical and geological bias

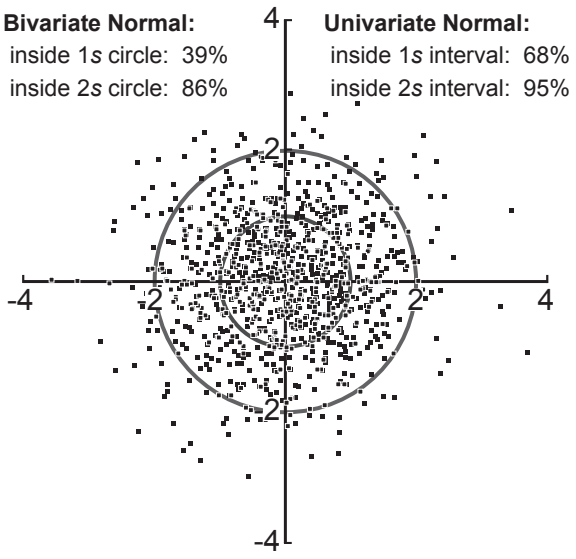

Figure 6. A bivariate normal distribution plot highlighting how little data (39%) falls within a 1*s* uncertainty ellipse. It is therefore recommended to always plot data point uncertainty ellipses at 2*s* within which the majority of data (86%) are contained.

between studies is limited to the 1–2% level, and progress requires improved measurement uncertainty to resolve these. Since a key benefit of *in situ* techniques such as LA-ICP-MS is the achievable spatial resolution, ablation of more material in an attempt to improve precision is not favoured (and could lead to the homogenisation of variability). For a population of data points with MSWD = 1, small levels of bias below the data point uncertainty level cannot be resolved and hence this uncertainty level constrains knowledge of the true population distribution (i.e., Gaussian or not). The MSWD (or reduced chi-squared statistic) is used to evaluate the fundamental assumption that the data included in a weighted mean are all measurements of a single true value. However, LA-ICP-MS U-Pb data, like data from arguably every other analytical method and chronometer, are limited in their ability to test this assumption. Because the precision of LA-ICP-MS U-Pb data is *ca.* 1%, this method can easily resolve discrepancies between data points that are much larger than this level of precision. However, resolving smaller-scale scatter requires discriminating MSWD values close to unity. While there are well-established confidence intervals for the MSWD, which depend on *n*, the number of data points (Wendt and Carl 1991), application of these depends strongly on the quality of the estimated uncertainties. If all of the uncertainties are estimated correctly, then MSWD values within acceptable limits can reliably be interpreted as evidence against heterogeneity. Unfortunately, difficult-to-quantify random and systematic sources of uncertainty abound in LA-ICP-MS, from variable down-hole ablation rates between samples, to uncertain initial common Pb contamination, to excess scatter in the reference data during a session. Slightly overestimating these uncertainty contributions can lead to MSWD values much closer to unity than truly reflected by the data, erroneously accepting the hypothesis that the data are repeated measurements of the same true value. This may tempt the user to allow the essentially unlimited ($\sim \sqrt{n}$) reduction in uncertainty in quantifying the sample uncertainty. This limitation is not unique to LA-ICP-MS U-Pb data. All geochronology and isotope tracer techniques are limited as to their level of interpretation by their data point uncertainties, and this applies to lower and higher precision techniques, whether the data are U-Pb or some other isotope system (e.g., Hf). To take weighted means of high *n* data sets without careful consideration of uncertainty quantification and categorisation as random vs. systematic therefore risks the result becoming inaccurate (with the defined uncertainty becoming less than the measurement bias) as illustrated earlier using the example from Sláma *et al.* (2008). As such, total (i.e., final age) uncertainties for a population cannot be quantified using a weighted mean calculation but must be further propagated to account for systematic uncertainty components.

The reporting of LA-ICP-MS U-(Th-)Pb data

A minimum amount of information (metadata) and (analytical) data must be reported for the assessment of data quality in any peer-reviewed publication and to demonstrate that the data quality is appropriate to support the interpretation made (Potts 2012a). Egli *et al.* (2003) described minimum requirements for the reporting of analytical data for environmental samples. They added that these may not be sufficient, depending on the nature of the work, and that adaptation may be needed for special project types. For LA-ICP-MS U-(Th-)Pb data to be evaluated appropriately in the context of the nature of the samples, comprehensive details about data acquisition and processing must be supplied. Along with knowledge of the analytical set-up used and the data processing method employed, information such as the ion beam size measured, elemental concentration, common Pb content and all relevant ratio data should be reported. This enables comprehension of the limitations of the analyses with respect to the measurement of ion beams and interference corrections for difficult samples, for example, young and/or low concentration materials. Provision of information regarding analytical set-up, such as details of laser model and ablation cell geometry, allows the reader/reviewer to ascertain the likely time and spatial resolution of the data. For example, high time resolution dissection of laser ablation data requires low (effective) volume, fast washout laser ablation cells and set-up, and this capability needs to be clearly demonstrated.

It is recommended that the following data and metadata tables are included in any manuscript containing LA-ICP-MS U-(Th-)Pb data. These tables should not substitute wholly for methodology text in the manuscript but instead provide a point of reference where these details can be readily found and stored online for longevity. In this way, interested readers can scrutinise in depth the veracity of the data, attempt to replicate them where appropriate and have the information available to them to answer relevant analytical quality questions about the data set which impact on the geological interpretation. Storage of complete data sets and metadata online should not be an impediment to the appropriate documentation of our science.

Reporting of metadata

Table 3 illustrates the recommended minimum metadata types to be submitted for publication with some example metadata. It is not intended that the information to be given as metadata be prescribed, but this should be as accurate as known or stated as 'not available' if appropriate.

Table 3.
Recommended reporting template (metadata) for LA-ICP-MS U-(Th-)Pb data. Metadata shown are for example only

Laboratory and Sample Preparation	
Laboratory name	Dept of Earth Science, University of Everywhere
Sample type/mineral	Detrital zircons
Sample preparation	Conventional mineral separation, 1 inch resin mount, 1 μm polish to finish
Imaging	CL, FEI Quanta600, 10 nA, 17 μm working distance
Laser ablation system	
Make, Model and type	ESI/New Wave Research, UP193FX
Ablation cell and volume	In-house built low volume cell, volume *ca.* 4 cm^3
Laser wavelength (nm)	193 nm
Pulse width (ns)	4 ns
Fluence (J cm^{-2})	2.5 J cm^{-2}
Repetition rate (Hz)	5 Hz
Ablation duration (s)	40 s
Ablation pit depth/ablation rate	16 mm pit depth, measured using an optical microscope, SEM and interferometry, equivalent to 0.08 μm/pulse
Spot diameter (μm) nominal/actual	25 μm/32 μm
Sampling mode/pattern	Static spot ablation
Carrier gas	100% He in the cell, Ar make-up gas combined using a Y-piece 50% along the sample transport line to the torch.
Cell carrier gas flow (l min^{-1})	0.8 l min^{-1}
ICP-MS Instrument	
Make, Model and type	Nu Instruments, Nu Plasma HR, MC-ICP-MS
Sample introduction	Ablation aerosol combined with co-aspiration of desolvated Tl-^{235}U tracer
RF power (W)	1300 W
Make-up gas flow (l min^{-1})	Sourced from Nu Instruments DSN-100 desolvating nebuliser. Neb pressure 24 psi (estimated at 0.7 l min^{-1}) Ar.
Detection system	mixed Faraday-multiple ion counting array
Masses measured	202–207, 235, 238
Integration time per peak/dwell times (ms); quadrupole settling time between mass jumps	200 ms for each isotope
Total integration time per output data point (s)	~ 1.2 s (N.B. this should represent the time resolution of the data)
'Sensitivity' as useful yield (%, element)	0.4% U ((#ions detected/#atoms sampled)*100; Schaltegger *et al.* 2015)
IC Dead time (ns)	6, 9 and 7 ns IC0, IC1 and IC2 resp.
Data Processing	
Gas blank	30 s on-peak zero subtracted
Calibration strategy	91500 used as primary reference material, Plešovice and GJ1 used as secondaries/validation
Reference Material information	91500 (Wiedenbeck *et al.* 1995) Plešovice (Sláma *et al.* 2008) GJ1 $^{206}Pb/^{238}U$ 0.097877 ± 0.07%, $^{207}Pb/^{206}Pb$ 0.060171 ± 0.08% (in-house CA-TIMS, this study)
Data processing package used/Correction for LIEF	Nu Instruments Nu Plasma TRA software and in-house spreadsheet for data normalisation, uncertainty propagation and age calculation. LIEF correction assumes reference material and samples behave identically.
Mass discrimination	Tl-U tracer solution used for initial mass bias correction with $^{207}Pb/^{206}Pb$ and $^{206}Pb/^{238}U$ additionally normalised to reference material
Common-Pb correction, composition and uncertainty	No common-Pb correction applied to the data.
Uncertainty level and propagation	Ages are quoted at 2*s* absolute, propagation is by quadratic addition. Reproducibility and age uncertainty of reference material and common-Pb composition uncertainty are propagated where appropriate.
Quality control/Validation	Plešovice – Wtd ave $^{206}Pb/^{238}U$ age = 338 ± 3 (2*s*, MSWD = 0.9, n = 8) GJ-1 – Wtd ave $^{206}Pb/^{238}U$ age = 602 ± 5 (2*s*, MSWD = 1.1, *n* = 7) Systematic uncertainty for propagation is 2% (2*s*).
Other information	Depth profiling and single-pulse ablation studies used a low-volume ablation cell, sample line of 3 m from ablation cell to torch and a 20 s wait time between ablations. Cell washout time was *ca.* 0.8 s to 1% of peak signal.

This reporting template is available for download on www.Plasmage.org.

Table 3 is divided into five sections – laboratory and sample preparation, information about the laser ablation system, information about the ICP-MS instrument, details of the data processing approach and any other relevant information.

Metadata relating to the laboratory and sample preparation methods are straightforward and that which are commonly provided, although the addition of details of the imaging methods and settings used is also useful. Commonly, details provided in publications to describe the laser ablation system and set-up are too sparse to allow proper assessment of the spatial and temporal resolution of the data. Along with the make and model of the laser, metadata regarding the ablation cell type and/or volume are important in understanding the likely time resolution achievable by the set-up. Details of laser wavelength, pulse width, fluence, repetition rate, ablation duration, pit depth, spot size, sampling mode and carrier gas are also important to understand, or indeed calculate, the spatial resolution of the reported set-up with respect to those interpretations being made in the manuscript. Details regarding the ICP-MS instrument are largely straightforward and those commonly reported on submission of a manuscript but, additionally, information relating to the integration (or dwell) times used and the integration (or sweep) times per data point output allow the reader/reviewer to better comprehend and assess the true time (and therefore spatial) resolution of the reported data and the actual number of counts detected per integration.

Reporting of analytical data

Table 4 illustrates the recommended minimum analytical data to be submitted for publication. This records details of the sample, ablation signal, concentration, proportion of common Pb, and Pb-Pb, U-Pb and Th-Pb (if measured) isotope ratios, with and without common Pb correction if appropriate, the date and concordance of the data points. The size of at least one ion beam signal should be included to allow all the others to be estimated via the ratios reported. The measured ion beam sizes and knowledge from the metadata table of the detectors used for the different ion beams allow the reader/reviewer to assess the reported precision levels and the likely analytical limitations within the data. Proportion of common Pb within the analysis can be expressed as 'f206c' - the proportion of the ^{206}Pb ion beam that is non-radiogenic Pb, calculated as:

$$\left(^{206}Pb^{204}Pb_{model}/^{206}Pb^{204}Pb_{measured}\right) \times 100 \qquad (1)$$

where $^{206}Pb^{204}Pb_{model}$ = $^{206}Pb/^{204}Pb$ ratio (e.g., Stacey and Kramers 1975) at the apparent (non-common Pb corrected) $^{207}Pb/^{206}Pb$ age. Expressed in this way, laser ablation U-(Th-)Pb data can be compared readily to the established reporting protocol of the SIMS community, which represents a direct analogue of the data produced by LA-ICP-MS. Reporting of ratios in a configuration ready for plotting as a Tera-Wasserburg (1972) plot (without common Pb correction) as well as a Wetherill (1956) plot (with common Pb correction if made) with a correlation coefficient (rho) allows the reader/reviewer to more easily replicate the plots described in the submitted manuscript instead of requiring them to recalculate ratios and rho values which could lead to errors in rearranging data. Data are best submitted as a spreadsheet or in a PDF format readily importable into a spreadsheet for easy use and interrogation. The footnotes should describe the uncertainty level on the concentration estimates, highlight which data are/are not corrected for common Pb, how the concordance values have been calculated, the systematic uncertainty components and their values, and any relevant references, for example, the source of the decay constants, $^{238}U/^{235}U$ and especially, the source of the primary reference values used for normalisation.

Validation

One or more validation (or secondary reference) materials should always be analysed during a measurement session, and the results reported with the sample data. The validation material is a reference material analysed and processed as an unknown. The submission of results for one or more validation materials is considered a prerequisite of the publication process, in order to demonstrate accuracy of the data set and the level of total uncertainty for recognised, well-characterised materials. At the very least, the validation results should be stated in Table 3 and cited in the manuscript. Ideally, data for one or more validation materials analysed at the same time as the samples should be included with the sample data set and stored as supplementary information (Potts 2012a). Without validation, the reader/reviewer is unable to assess the accuracy of the data set, and its credibility and usefulness is greatly devalued. The compilation of these data over time is the source of the ε' long-term excess variance required in the uncertainty propagation protocol.

Summary of recommendations

(1) Use the metadata and analytical table formats shown (Tables 3 and 4) when submitting a manuscript containing LA-ICP-MS U-(Th-)Pb data to a journal. These tables can be obtained from online

Table 4.
Recommended data-reporting template for laser ablation ICP-MS U-Th-Pb data: typical table for zircon

20th July 2016, Dept. Earth Sci., Univ. of everywhere[a]								Data for Tera-Wasserburg plot[b]						Data for Wetherill plot[c]								Dates[c]										% conc[d]
Identifier	Comments	f206c	^{206}Pb (mV)	U µg g^{-1}	Th/U	^{206}Pb/^{204}Pb	1 *s* %	^{238}U/^{206}Pb	1 *s* %	^{207}Pb/^{206}Pb	1 *s* %	^{208}Pb/^{206}Pb	1 *s* %	^{207}Pb/^{235}U	1 *s* %	^{206}Pb/^{238}U	1 *s* %	Rho	^{208}Pb/^{232}Th	1 *s* %	^{207}Pb/^{206}Pb	2 *s* abs	2 *s*$_{sys}$ abs	^{206}Pb/^{238}U	2 *s* abs	2 *s*$_{sys}$ abs	^{207}Pb/^{235}U	2 *s* abs	2 *s*$_{sys}$ abs	^{208}Pb/^{232}Th	2 *s* abs	2 *s*$_{sys}$ abs	
GJ1		bd	2.4	301	#N/A	#N/A	#N/A	10.23	1.5	0.05956	0.52	#N/A	#N/A	0.8022	1.6	0.09772	1.5	0.94	#N/A	#N/A	588	11	13	601	17	21	598	14	17	#N/A	#N/A	#N/A	102.3
GJ1		bd	2.4	294	#N/A	#N/A	#N/A	10.11	1.3	0.05986	0.53	#N/A	#N/A	0.8164	1.4	0.09896	1.3	0.93	#N/A	#N/A	599	12	13	608	15	19	606	13	16	#N/A	#N/A	#N/A	101.6
GJ1		bd	2.4	301	#N/A	#N/A	#N/A	10.20	1.3	0.05988	0.53	#N/A	#N/A	0.8089	1.4	0.09802	1.3	0.93	#N/A	#N/A	599	12	13	603	15	19	602	13	16	#N/A	#N/A	#N/A	100.6
GJ1		bd	2.5	314	#N/A	#N/A	#N/A	10.40	1.1	0.06033	0.57	#N/A	#N/A	0.7998	1.2	0.09619	1.1	0.89	#N/A	#N/A	616	12	14	592	12	17	597	11	14	#N/A	#N/A	#N/A	96.2
GJ1		bd	2.5	305	#N/A	#N/A	#N/A	10.26	1.3	0.06021	0.53	#N/A	#N/A	0.8090	1.4	0.09749	1.3	0.93	#N/A	#N/A	611	11	13	600	15	19	602	13	16	#N/A	#N/A	#N/A	98.1
GJ1		bd	2.5	305	#N/A	#N/A	#N/A	10.10	1.0	0.06010	0.48	#N/A	#N/A	0.8202	1.1	0.09901	1.0	0.91	#N/A	#N/A	607	10	12	609	12	17	608	10	14	#N/A	#N/A	#N/A	100.2
GJ1		bd	2.5	299	#N/A	#N/A	#N/A	10.13	1.2	0.06012	0.51	#N/A	#N/A	0.8181	1.3	0.09874	1.2	0.92	#N/A	#N/A	608	11	12	607	14	18	607	12	15	#N/A	#N/A	#N/A	99.9
GJ1		bd	2.4	299	#N/A	#N/A	#N/A	10.05	1.2	0.05951	0.51	#N/A	#N/A	0.8157	1.3	0.09945	1.2	0.92	#N/A	#N/A	586	11	13	611	14	18	606	12	15	#N/A	#N/A	#N/A	104.3
GJ1		bd	2.6	315	#N/A	#N/A	#N/A	10.19	1.1	0.06018	0.55	#N/A	#N/A	0.8141	1.3	0.09815	1.1	0.90	#N/A	#N/A	610	12	13	604	13	17	605	11	15	#N/A	#N/A	#N/A	98.9
GJ1		bd	2.5	305	#N/A	#N/A	#N/A	10.31	1.3	0.05995	0.56	#N/A	#N/A	0.8011	1.4	0.09695	1.3	0.92	#N/A	#N/A	602	12	14	597	15	19	597	13	16	#N/A	#N/A	#N/A	99.1
GJ1		bd	2.6	314	#N/A	#N/A	#N/A	10.17	1.3	0.06051	0.54	#N/A	#N/A	0.8203	1.4	0.09837	1.3	0.92	#N/A	#N/A	622	12	13	605	15	19	608	13	16	#N/A	#N/A	#N/A	97.3
GJ1		bd	2.5	310	#N/A	#N/A	#N/A	10.23	1.4	0.05980	0.53	#N/A	#N/A	0.8053	1.5	0.09772	1.4	0.94	#N/A	#N/A	596	12	13	601	16	20	600	14	16	#N/A	#N/A	#N/A	100.8

Decay constants of Jaffey et al. (1971) used. bd, below detection; #N/A, not available. Uncertainties quoted without components related to systematic error unless otherwise stated. Total systematic uncertainties (s_{sys}): ^{206}Pb/^{238}U = 2.0%, ^{207}Pb/^{206}Pb = 0.55% (2*s*).

[a] Concentration uncertainty *ca.* 20%.

[b] Data not corrected for common Pb.

[c] Data corrected/not corrected for common Pb.

[d] Concordance calculated as (^{206}Pb-^{238}U age/^{207}Pb-^{206}Pb age)*100.

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supporting information (this paper, Tables S3 and S4) or from www.PlasmAge.org. Submit data tables so that they can be handled easily by the reader/reviewer in a spreadsheet.

(2) Use the new Hiess *et al.* (2012) $^{238}U/^{235}U$ values where determined for the reference material used, or in their absence, the quoted mean for terrestrial materials of 137.818 ± 0.045 (2*s*).

(3) Use the uncertainty propagation protocol as described herein.

(4) Present validation data, or at least quote the validation result, with the sample data submitted. Ideally store online with the sample data.

(5) Always plot data points at 2*s* and report date and age uncertainties in text and tables at 2*s*. When quoting population ages (or dates), state the MSWD value and *n*, obtained on the weighted mean calculation prior to propagation of uncertainties related to systematic errors. (Note that 'MSWD of concordance' used in Ludwig 2012 is not the same as the weighted mean MSWD discussed here).

(6) Compare data within igneous and metamorphic populations or within detrital samples as *dates*, that is, without s_{sys}. Compare data between analytical sessions or publications with s_{sys}.

(7) Never take a weighted mean of a set of data points that include s_{sys}.

(8) Use ID-TIMS reference ratios (with/without common Pb or ^{230}Th correction as appropriate to the LA data being normalised) specific to the isotope ratio of interest, not an assumed-age equivalent calculated ratio. For most current practices, this entails using ratio-specific reference values without common Pb or ^{230}Th corrections from non-chemically abraded materials.

(9) Quote age uncertainties with two components, for example, Age ± α/β (= without/with propagation for s_{sys}).

Future directions

As a community of LA-ICP-MS U-(Th-)Pb practitioners, we will continue to discuss and make recommendations to resolve some of the more difficult challenges that affect the quality of our data and ability to interpret them. The impact of different data processing algorithms is currently under investigation, as is the extent of systematic bias between laboratories as illustrated through long-term data sets of reference materials. The mapping of the effect of variation in gas flow across ablation cells on U-Pb fractionation behaviour is required knowledge for all practitioners to improve consistency of results. More research to better quantify the effect and utility of thermal annealing/chemical abrasion for zircon LA-ICP-MS U-Pb work is required. New investigations will need to focus on improved procedures for correction of LIEF and common Pb, and further developments are required in high time and spatial resolution analysis and, perhaps most importantly, dating of accessory phases other than zircon.

Conclusions

Through community collaboration and discussion, we have defined new protocols for the calculation of uncertainty and for the interpretation and reporting of LA-ICP-MS U-(Th-)Pb data. These will help harmonise data processing practices and move the community towards achieving the goal of improving the present limits to precision and accuracy that currently restrict LA-ICP-MS geochronology. We have interrogated our data to better understand its true form, the impact of the acquisition parameters through the data processing procedure, identified the component uncertainties within the data and identified an improved propagation protocol for these.

New guidelines are defined for the use of weighted mean statistics and the propagation of systematic uncertainty components, allowing better quantification of age uncertainty and comparison of data at different uncertainty levels within and between acquisition sessions as well as between laboratories and different decay systems. This allows the geochronology community to have much greater confidence in interpreting age differences based on LA-ICP-MS data. Critically, this work does not address possible matrix effect-related biases but will allow data to be viewed appropriately, with the correct uncertainties, in order that any matrix effects can be better resolved.

Treating our data in this open, transparent and objective manner (as advocated in Potts 2012a and Schoene *et al.* 2013) will highlight systematic differences more clearly and allow refinement of analytical practice and set-up, ultimately contributing to the improvement of the combined uncertainty for the method.

As part of this process, it is imperative that data are reported appropriately for thorough peer-review and robust interpretation by readers. New templates for metadata and analytical data are defined which are intended to constitute the minimum required reporting standards. In order to achieve our community goals and improve our science, all involved in the LA-ICP-MS geochronology community (data producers, users, editors, reviewers and readers) can play a part in supporting the robust implementation of these

minimum requirements. Reviewers and journals should feel empowered to insist on such standards, and indeed we would like to encourage all journals to take up these proposals and ask all reviewers to implement them, even refusing the review and publication of manuscripts without them (Egli *et al.* 2003). This change, of insisting on the more robust and thorough documentation of our science, will improve published LA-ICP-MS geochronology data and therefore the accuracy and age resolution with which we can interpret our data.

Acknowledgements

Sadly, our friend and colleague Prof. Jan Košler passed away before the completion of this manuscript. Jan was a key driving force of this effort and his input and comradeship are dearly missed by us all. We dedicate this paper to him for his many years of effort on this initiative. The authors and co-ordinators of the LA-ICP-MS U-(Th-)Pb Network would like to thank the sponsors of the workshops we have held to date that have enabled discussions on these points and resulted in this manuscript. These include instrumentation manufacturers, academic and government institutions. NSF is particularly thanked for supporting Grant number EAR-0930223 (awarded to J.F. Bowring) that has been instrumental in the outcomes and for supporting Grant number EAR-1338583 (awarded to G. Gehrels). The International Association of Geoanalysts and members of the EARTHTIME initiative are thanked greatly for their ongoing support. All participants of the workshops (100 different attendees/online contributors across the four workshops) are thanked for contributing to the process and inputting their views and comments during the workshops and subsequent discussions. Thanks also to our collaborators in the SIMS and ID-TIMS communities who have been instrumental in helping us find a way forward whilst learning from their experiences and to Jiri Sláma for the design and maintenance of the PlasmAge.org website. MH thanks Elena Belousova for providing the GJ1 zircon material, Richard Stern and Nicole Rayner for the 'Stern' monazite, Anne-Magali Seydoux-Guillaume for the Moacyr monazite and Craig Storey for the Ontario 2 titanite. The authors thank Thomas Meisel for editorial handling and two anonymous reviewers for providing constructive criticism that helped clarify the manuscript.

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Supporting information

The following supporting information may be found in the online version of this article:

Table S1. New ID-TIMS data for zircon reference materials GJ1, 91500 and Mud Tank with Plešovice data from Sláma *et al.* (2008) updated with the current EARTHTIME tracer calibration.

Table S2. Reference values for some reference materials used commonly in LA-ICP-MS U-Pb dating.

Table S3. Recommended reporting template (metadata) for LA-ICP-MS U-(Th-)Pb data.

Table S4. Recommended reporting template (analytical) for LA-ICP-MS U-(Th-)Pb data.

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